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COMPLETE SPECIFICATION

Process for the preparation of Primary Alcohols

We, HENKEL & CIE G.M.B.H., a German Company, of 67, Henkelstrasse, Duesseldorf-Holthausen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of primary alcohols which preferably contain practically no secondary alcohols, by catalytic hydrogenation of aliphatic monoepoxides having a terminal epoxide group.

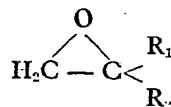
Catalytic hydrogenation of aliphatic monoepoxides with the epoxide group in the terminal position, to the corresponding primary alcohols has already been proposed. Among others, nickel, cobalt, iron and copper have been proposed as catalysts. According to the experiments previously described in the literature, nickel is much preferred as the catalyst. The alcohols prepared therewith, however, always contain certain amounts of secondary alcohols. Cobalt has only previously been used in the hydrogenation of lower aliphatic epoxides containing not more than 4 carbon atoms in the molecule; the results obtained therewith are said to be equivalent to those attained with nickel.

In the application of this process to higher aliphatic epoxides with terminal epoxide groups containing 7 to 22 carbon atoms in the molecule, therefore, the formation of relatively large quantities of secondary alcohols would be expected, which would be undesirable in the conversion of these alcohols into esters utilisable as plasticisers or into sulphates utilisable as surface-active substances. It was therefore very surprising when it was found that aliphatic monoepoxides with terminal epoxide groups and containing 7 to 22 carbon atoms in the molecule can be catalytically hydrogenated to primary alcohols which contain practically no secondary alcohols, when

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this hydrogenation is carried out using cobalt, iron, osmium or mixtures thereof as catalysts. In order to limit the amount of secondary alcohol formed the amount of cobalt, iron, osmium or mixtures thereof is at least 50% by weight of the metal in the catalyst, i.e. the amount of catalytically active metal present in the catalyst, whether as a mixture of metals or as a single metal, is at least 50% by weight of the metal in the catalyst.

The aliphatic monoepoxides with terminal epoxide groups serving as starting materials comprise compounds of the following formula:



in which R₁ represents an aliphatic hydrocarbon residue with 5—20, preferably 8—16, carbon atoms. R₂ is preferably a hydrogen atom; but may also represent aliphatic hydrocarbon residues with 1—10 carbon atoms (see "Epoxydverbindungen und Epoxydharze", Berlin, 1958, page 235), in which case the epoxide to be treated according to the invention should contain not more than 22, and preferably not more than 18, carbon atoms in the molecule.

The metals cobalt, osmium or iron serving as catalysts may be used in the usual way, i.e. as finely divided metals which may be deposited on carriers and if desired are obtained, for example, from the oxides, hydroxides, carbonates, bicarbonates, formates, nitrates of the said metals by thermal decomposition in the presence of hydrogen and/or by reduction. However, the metals may also be employed as finely-divided Raney metals. Suitable carriers are solid substances inert under the reaction conditions, for example,

aluminium oxide, silicic acid and powdered pumice. The addition of small amounts of thorium, magnesium or alkali metals as activator has proved satisfactory.

5 The reduction of the metal compounds to the catalytically active metals may take place immediately before the hydrogenation, when the metal compounds, either deposited on the above carriers or alone, are moistened if desired with inert solvents. Suitable inert solvents are hydrocarbons or alcohols, and preferably those which, owing to their boiling point, can easily be separated from the primary alcohols to be prepared. But the alcohols
10 formed as end products of the process according to the invention may also serve as inert solvents in the reduction of the metal compounds to the catalytically active metals.

15 The reduction of the terminal epoxides to the primary alcohols may be effected at temperatures in the range of 100° to 250°C, and it is preferred to work in the range of temperature from 120 to 200°C.

20 In a preferred method of carrying out the reaction, the epoxide serving as starting material is heated with hydrogen at the reaction temperature in the presence of the catalyst. The process may be carried out continuously or discontinuously. In the discontinuous process, the catalyst is usually added to the epoxide to be treated, and is used in amounts of at least 0.5% by weight of the epoxide to be reduced, and preferably in amounts of 1—10% by weight of epoxide.
25 The material is then heated with stirring and the hydrogen for the hydrogenation is passed into the reaction vessel, the operation being suitably carried out at increased pressures up to, say, 400 atmospheres, and preferably at
30 20—300 atmospheres, and if desired the hydrogen may be recirculated. When the reaction is finished, the catalyst is filtered off and if desired the crude product obtained is worked up.

35 In the continuous operation of the reaction, the epoxide to be reduced and the hydrogen are usually passed over the stationary catalyst. In this case the amount of catalyst present in the reaction vessel may at times be substantially greater than the amount of epoxide and already formed alcohol present in the reaction vessel. The amount of catalyst, for example, may amount to ten times, one hundred times or five hundred times the amount of epoxide plus alcohol.
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The continuous reaction may be carried out under conditions in which the epoxide to be hydrogenated is present largely or entirely in the gaseous state. This can be effected particularly easily in the case of lower boiling members of the epoxides to be treated according to the invention, e.g. with those which boil at temperatures up to 160°C under normal pressure. These may be passed over the stationary catalyst in the gaseous state, together
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with the hydrogen, possibly under slightly increased pressure. It is obviously also possible to work at higher pressures, i.e. at the pressures indicated above, so that large parts of the epoxide to be treated are present in the liquid state. 70

The hydrogenation of the epoxides may also be effected over finely divided catalyst forming a fluidised bed, especially when the epoxide and the alcohol formed therefrom are present under the selected reaction conditions largely or entirely as vapour. 75

In some cases it may be desired to use the epoxide in a dilute state. Suitable diluents are inert solvents especially hydrocarbons or alcohols, which can easily be separated from the reaction product, e.g. by distillation. The quantity of solvent may amount to up to ten times the weight of the epoxide. 80

It has been found that the hydrogenation products obtained according to the invention by use of cobalt or iron as catalysts contain practically no secondary alcohol, but sometimes small amounts of hydrocarbons. This is an advantage insofar as, in contrast to the secondary alcohols, the hydrocarbons can be separated without special difficulty from the primary alcohols, for example, by distillation or extraction. 85
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Even if the primary alcohols containing a small amount of hydrocarbons, obtained according to the invention are further treated, the separation of the components of the mixture does not present the same technical difficulties, as is the case in the treatment of primary alcohols containing a corresponding amount of secondary alcohols. In the preparation of plasticisers, the secondary alcohols are also esterified, even if not as rapidly as the primary alcohols, but the esters of secondary alcohols formed are not thermally so stable as those derived from primary alcohols, so that when the esters are incorporated in the high molecular substance to be plasticised, decomposition may occur. 95
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More rigorous reaction conditions have to be used for sulphating higher primary fatty alcohols than the corresponding secondary alcohols. If the primary alcohols contain secondary alcohols, discoloured decomposition products are formed under the conditions required for the sulphation of the primary alcohols, while paraffins which may be present are inert and can be easily separated from the alkyl sulphate formed. 115
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It has now also been found that the formation of hydrocarbons is reduced if nickel is added to the cobalt catalyst. The amount of nickel should not be greater than 50% by weight of the mixture of nickel and cobalt, and preferably not greater than 35% by weight of this mixture. 125

EXAMPLES

The straight chain aliphatic mono epoxides with chains of 8, 10, 12 and 16 carbon atoms 130

used as starting materials were obtained by epoxidising the corresponding pure olefines with terminal double bonds with peracetic acid

and separating the epoxides obtained from the epoxidation product by distillation. The epoxides had the following properties:

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TABLE 1

Properties of the terminal epoxides which were treated

Characteristics	Chain length of the epoxide			
	C ₈	C ₁₀	C ₁₂	C ₁₆
found	1.4202	1.4302	1.4365	1.4458
n_D^{20} literature	1.4193	1.4288	1.4356	—
B.p. in °C./mm Hg.	80/40	90/11	93/3.5	119/0.4
% (wt) of epoxide oxygen				
Found	12.39	10.23	8.64	6.65
Calculated	12.48	10.24	8.68	6.66

The catalyst used in experiment 1 was prepared by the following process: 198 g of Co(NO₃)₂·6 H₂O, 25.4 g. of Mg(NO₃)₂·6H₂O and 4.46 g of Th(NO₃)₄·3H₂O were dissolved in one litre of distilled water, heated to boiling and were added to a boiling solution of 104 g of Na₂CO₃ in one litre of distilled water, during which the mixture was vigorously stirred. 30 seconds after running in the nitrate solutions, 78 g of kieselguhr (purified by washing with hydrochloric acid and igniting) were added with vigorous stirring. After the addition of the kieselguhr, stirring was continued for a minute and the water was filtered off by suction. The filter residue was then washed with two litres of distilled water. The solid filter cake was then suspended in four litres of water for 15 minutes with vigorous stirring and filtered again. This purifying operation was repeated twice. The filter cake was then dried at 110°C for 14 hours and after this was pulverised. The granular fraction sifted out in sieves of between 1 and 3 mm inside width was used for further treatment. This fraction was reduced with hydrogen, which had been dried over sulphuric acid, in a fire-proof glass tube situated in a horizontal tube furnace heated at 400—450°C. 450 litres of hydrogen were passed over for the reduction, which lasted for six hours. The hydrogen was then driven out by nitrogen and the reduced catalyst was allowed to cool in the stream of nitrogen. The pyrophoric catalyst, which contained 0.2% by weight of sodium and 0.36% by weight of potassium, was drawn off in a current of carbon dioxide.

The preparation of the catalysts used in the experiments 2—9 was carried out in an analogous way. In the case of catalysts of

different composition, either the magnesium or the thorium was omitted or the cobalt was replaced partially or completely by the equivalent molecular percentage of the metal indicated therein. The catalysts without carriers were also prepared by this general instruction; only the carrier was omitted. In some cases kieselguhr was replaced by the same amount of weight of another carrier.

The Raney metal catalysts used in the experimental series 10 and 11 were prepared according to the instructions given in "Organic Syntheses", Vol. 21, New York 1941, pages 15—17.

For the preparation of the cobalt-manganese catalyst used in the experimental series 13, 94 kg of cobalt sulphate and 18 kg manganese sulphate were dissolved in 2500 litres of water, heated to 55°C and precipitated at 55°C by addition of a solution at 55° of 80 kg of anhydrous soda in 2500 litres of water. The precipitate, after thoroughly filtering by suction, was washed and dried at 70°C. The product was ground and, after mixing with 3% by weight of graphite, was tabletted and reduced.

In the case of the experimental series 1—5 and 7—13, the hydrogenation was accomplished as follows: 40 g of epoxide and 2 g of catalyst were placed in an autoclave and hydrogen was introduced until the pressure was 40 atmospheres. It was then heated to 150°C, when the pressure had increased to 65 atmospheres.

Using the iron catalyst (experimental series 6), hydrogen at a pressure of 100 atmospheres was introduced in the cold and the reaction temperature raised to 190°C.

The catalyst was filtered off and the

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reaction mixture was distilled in a spinning band column. The intermediate fractions obtained during the distillation in the spinning band column were separately collected. The pure fractions isolated by distillation had the

characteristics given in Table 2. The intermediate fractions were not investigated more closely; the amount of each was equal to half the pure fractions between which they had been collected.

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TABLE 2

Properties of the distillate fractions of the epoxide hydrogenation products

No. of carbons	Chemical designation	b.p. °C./mm Hg.	n_D /°C.	OH Value	% epoxide oxygen (wt.)
8	Paraffin	45/40	1.3982/20	0	
8	Epoxide	83/40	1.4193/20	—	
8	sec. alcohol	101/40	1.4261/20	416	
8	primary alcohol	115/40	1.4292/20	427	
10	paraffin	61/12	1.4138/20	0	
10	epoxide	93/12	1.4287/20	—	9.81
10	sec. alcohol	106/12	1.4349/20	343	
10	primary alcohol	119/12	1.4380/20	350	
12	paraffin	95/12	1.4202/25	0	
12	epoxide	123/12	1.4340/20	—	8.59
12	sec. alcohol	130/12	1.4390/25	292	
12	primary alcohol	142/12	1.4413/25	293	
16	paraffin	132/4		0	
16	epoxide	155/4	1.4458/20		6.29
16	sec. alcohol	158/4		218	
16	primary alcohol	166/4		228	

The yields of hydrocarbon, possibly epoxide, secondary and primary alcohol obtained in the separate series of experiments are grouped in the following Table 3, these yields relating to the filtrate obtained after filtering off the

catalyst. Provided the sum of the yields is not 100%, the remainder corresponds to the sum of the loss occurring during the distillation and the distillation residue.

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TABLE 3
Results of hydrogenation experiments

Experi- mental series No.	Catalyst	Fractions obtained from hydrogenation product in % by wt.											
		C ₃			C ₁₀			C ₁₂			C ₁₆		
		Par- affin	sec. alcohol	prim alcohol	Par- affin	sec. alcohol	prim alcohol	Par- affin	sec. alcohol	prim alcohol	Par- affin	sec. alcohol	prim alcohol
1	Co Th Mg on kieselguhr	6	—	86	12	—	83	13	—	81	18	—	76
2	Ni Th Mg on kieselguhr	—(1)	32	64	—(1)	22	67	—(1)	23	70	3	25	68
3	Co on kieselguhr	7	—	82	14	—	80	17	—	77	19	—	74
4	Co on active carbon	27	—	51	43	—	43	47	—	46	51	—	45
5	Co Th Mg on Al ₂ O ₃	4	—	85	9	—	82	12	—	80	13	—	78
6	Fe Th Mg on kieselguhr	10	14(2)	52	12	—	75	22	—	71	15	53(2)	18
7	Co Th Mg	5	—	82	17	—	78	16	—	78	16	—	81
8	1/4 Ni 3/4 Co; Th Mg on kieselguhr	7	—(1)	80	4	—	86	21	—(1)	71	13	—	75
9	1/2 Ni 1/2 Co; Th Mg on kieselguhr	2	13	80	2	10	78	8	—	84	6	—	89
10	Raney Co	16	—	71	17	—	69	26	—	68	26	—	69

TABLE 3
Results of hydrogenation experiments

Experi- mental series No.	Catalyst	Fractions obtained from hydrogenation product in % by wt.											
		C ₈			C ₁₀			C ₁₂			C ₁₆		
		Par- affin	sec. alcohol	prim alcohol	Par- affin	sec. alcohol	prim alcohol	Par- affin	sec. alcohol	prim alcohol	Par- affin	sec. alcohol	prim alcohol
11	Raney Ni	-(1)	12	79	8	13	65	8	10	74	6	11	74
12	Commercial Fischer-Tropsch catalyst 80 c.c. C ₃ H ₅ OH	—	—	—	—	—	—	11	—	79	—	—	—
13	Mn	17	—	72	30	—	57	25	—	66	22	—	66

(1) Traces

(2) Unreacted epoxide

In the Table the action of cobalt- or iron-containing catalysts is compared with that of nickel catalysts. Moreover, experiments with platinum oxide, palladium oxide, palladium on active charcoal and a copper chromite catalyst were carried out; in all cases considerable amounts of secondary alcohol and/or hydrocarbon were formed during the reduction, some of which were larger than the amounts of the primary alcohol formed.

Experimental series 14:

An apparatus described by Ullmann: "Encyclopadie der technischen Chemie", 3rd Edition, Vol. VII (1956), page 447, was used for the continuous operation of the reduction. The hydrogen circulating pump, denoted therein by g had a feed performance of 25 litres of gas at the pressure prevailing in the apparatus. The reaction space was 800 cc. The reaction vessel was filled with 500 g of the tabletted mixture of cobalt and manganese carbonates before the start of the experiment. The catalyst was reduced under the conditions of the latter hydrogenation before the reduction of the epoxide. Then a mixture of dodecene epoxide and five times its amount by weight of cyclohexane was passed through; the throughput amounted to 100 c.c. per hour of mixture, and the residence time of the mixture in the reaction vessel amounted to about 6 seconds. The hydrogen pressure during the hydrogenation amounted to 270 atmospheres. 3 series of experiments were carried out at 115, 120 and 125°C.

The crude products obtained at the said temperatures were freed from the solvent and distilled.

The product obtained at 115°C yielded a first fraction 10.0% by weight consisting substantially of paraffin, an intermediate fraction consisting partly of unreacted epoxide, and a principal fraction of 83.5% by weight. This principal fraction had an OH value of 299 and contained only 0.1% by weight of unsaponifiable material. It consisted substantially of primary alcohol.

The product obtained at 120°C yielded during the distillation 10.4% by weight of paraffin first runnings, 3.8% by weight of intermediate fraction consisting substantially of unreacted epoxide, and 85.6% by weight of the principal fraction. This principal fraction represented the desired primary alcohol; it had an OH value of 300 and contained

0.1% by weight of unsaponifiable material.

The product obtained at 125°C yielded 11.3% by weight of paraffin first runnings, 5.2% by weight of an intermediate fraction (epoxide) and 83.0% by weight of a principal fraction. This principal fraction represented the desired primary alcohol; it had an OH value of 300 and contained 0.1% by weight of unsaponifiable material.

All alcohols were converted into the sulphates; in this the alcohols showed no difference in behaviour from the coconut fatty alcohol obtained by reduction of coconut fatty acid esters.

Experiment 15:

The dodecene oxide used in the experimental series 1—14 was hydrogenated under the conditions used in the series 1—13; 7 c.c. of a colloidal solution of osmium in acetone prepared according to Makowka (Berichte der deutschen chemischen Gesellschaft, Vol. 41 (1908), pages 943/944) were used as catalyst. 17% by weight of the distillate consisted of dodecane and 68% by weight of primary dodecanol; secondary dodecanol could not be detected.

Example 16

The apparatus described in the experimental series 14 served for the continuous operation of the reduction. The cobalt-magnesium-thorium catalyst was used, the preparation of which is described following Table 1. 402 g (= 690 c.c.) of the granular fraction screened between sieves of 2 and 4 mm inside width of mesh were placed in the reaction tube and with the catalyst were reduced by hydrogen (at 300 atmospheres) at 250°C in a period of 135 minutes.

The temperature in the reaction vessel was then reduced to 120°C, the hydrogen was replaced by a gaseous mixture at 300 atm, which contained hydrogen and nitrogen in the proportion by volume of 2:1, and 100 c.c. per hour of a mixture of 1 part by volume of dodecenoxide-1 and 5 parts by volume of cyclohexane were added. The reaction product collected in 24 hours was freed from cyclohexane by distillation and then 200 c.c. of the residue (= 162.5 g) were finely fractionated. The quantity of the fractions obtained and their characteristics are tabulated in the following table:

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Fraction	Chemical name	Quantity		B.p. °C./mm Hg	Characteristics	
		Wt. g	Wt. %		epoxide number	OH value
1	first runnings	1.7	1.0	78—91	0	32
2	Dodecane	17.9	11.0	91	0	0
3	Intermediate	3.2	2.0	91—136	—	—
4	Lauryl alcohol	135.0	83.1	136.5	0	300
Residue		1.6	1.0			
Loss		3.1	1.9			

On the assumption that half of the intermediate fraction (fraction 3) consisted of lauryl alcohol, the lauryl alcohol content of the reaction product amounted to 84% by weight. 10
 5 *Example 17*
 This was carried out like Example 16, but the composition of the gas mixture used for the hydrogenation was 1/3 H₂ and 2/3 N₂. 200 c.c. (=161.7 g) were used for the fine fractionation. The fractions obtained and their characteristics were:

Fraction	Chemical name	Quantity		B.p. °C./mm Hg	Characteristics	
		Wt. g	Wt. %		Epoxide value	OH value
1	First runnings	1.3	0.8	80 —91	—	—
2	Dodecane	19.1	11.8	91—91.5	0	3.2
3	Intermediate fraction	2.8	1.7	95—136	—	—
4	Lauryl alcohol	134.8	83.4	136.5	0	304
Residue		0.8	0.5			
Loss		2.9	1.8			

On the assumption that half the intermediate fraction (Fraction 3) consisted of lauryl alcohol, the reaction product contained about 84% weight of lauryl alcohol.

WHAT WE CLAIM IS:—

1. A process for the preparation of a primary alcohol which comprises hydrogenating an aliphatic monoepoxide having a terminal epoxide group and containing 7—22 carbon atoms per molecule in the presence of a metal catalyst which contains at least 50% by weight of cobalt, iron or osmium or at least 50% by weight of a mixture thereof.

2. A process as claimed in claim 1 in which the epoxide contains 10—18 carbon atoms per molecule.

3. A process as claimed in either claim 1 or claim 2 in which the catalyst also contains nickel and in which the amount of nickel is at most 50% by weight referred to metal present in the catalyst.

4. A process as claimed in claim 1 or claim 2 in which the catalyst also contains nickel and in which the amount of nickel is at most 35% by weight referred to metal present in the catalyst.

5. A process as claimed in any one of the claims 1 to 4 in which the hydrogenation is carried out at a temperature in the range 100 to 250°C.

6. A process as claimed in any one of the claims 1 to 5 in which the hydrogenation is

carried out at a temperature in the range 120—200°C.

5 7. A process as claimed in any one of the claims 1 to 6 in which the hydrogenation is carried out as a superatmospheric pressure up to 400 atmospheres.

10 8. A process as claimed in any one of claims 1 to 7 in which the hydrogenation is carried out at a pressure in the range 20—300 atmospheres.

9. A process for the preparation of a primary alcohol substantially as described hereinbefore with reference to any one of the examples 1, 3 to 10 and 12 to 17.

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